[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE ACTION OF THIOCYANOGEN UPON O,N-DISUBSTITUTED HYDROXYLAMINES AND PRIMARY AMINES[1]

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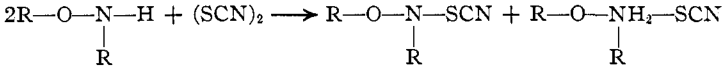
The action of thiocyanogen upon amines has been investigated by Söderbäck[2] and by Lecher, Wittwer and Speer.[3] Söderbäck studied the reaction with phenyl-, diphenyl- and dimethylphenylamine and, in each case, found that the thiocyanogen group entered the benzene ring para to the amino group. Lecher, Wittwer and Speer showed that in the case of the products formed with ammonia and with diethylamine, the thiocyanogen group attaches itself directly to the nitrogen atom. The purpose of this work was to extend the study of these reactions of thiocyanogen by investigation of the behavior of thiocyanogen with O,N-disubstituted hydroxylamines and with certain primary amines.

O,N-Disubstituted N-Thiocyanohydroxylamines

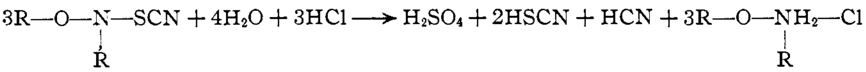
The action of thiocyanogen on O,N-disubstituted hydroxylamines corresponded to the action of thiocyanogen upon ammonia and diethylamine. Hydroxylamines with ethyl and benzyl groups were used for this purpose. They reacted with thiocyanogen as follows



$$2R{-}O{-}\underset{\substack{|\\ R}}{N}{-}H + (SCN)_2 \longrightarrow R{-}O{-}\underset{\substack{|\\ R}}{N}{-}SCN + R{-}O{-}\underset{\substack{|\\ R}}{NH_2}{-}SCN$$

The thiocyanohydroxylamines formed in this manner are not very stable compounds. O,N-diethyl-N-thiocyanohydroxylamine distilled from 45 to 46° at 2 mm. but decomposed rapidly when exposed to the air at room temperature. At 0° this substance showed no signs of decomposition after several hours. The corresponding O,N-dibenzyl compound was a white crystalline solid; m. p. 50–52°. At room temperature it could be kept for about forty-eight hours without signs of decomposition.

Hydrolysis of O,N-Disubstituted N-Thiocyanohydroxylamines.—The structure of these compounds was established by acid and by alkaline hydrolysis. Acid hydrolysis gave results which corresponded closely in form with those observed by Lecher, Wittwer and Speer in their investigations of similar amine derivatives.



$$3R{-}O{-}\underset{\substack{|\\ R}}{N}{-}SCN + 4H_2O + 3HCl \longrightarrow H_2SO_4 + 2HSCN + HCN + 3R{-}O{-}\underset{\substack{|\\ R}}{NH_2}{-}Cl$$

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[1] This paper is based upon a thesis submitted by Elmer E. Fleck to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Söderbäck, *Ann.*, **419**, 270 (1919).

[3] Lecher, Wittwer and Speer, *Ber.*, **56B**, 1104 (1923).

Bjerrum and Kirschner[4] have shown that the first step in the hydrolysis of thiocyanogen proceeded as follows

$$(SCN)_2 + HOH \longrightarrow HSCN + HOSCN$$

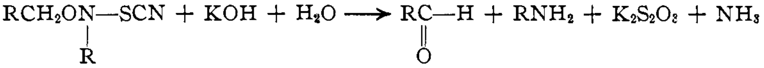
The hypothiocyanic acid then underwent auto-oxidation according to the following reaction

$$3HOSCN + HOH \longrightarrow 2HSCN + HCN + H_2SO_4$$

Since thiocyanic, hydrocyanic and sulfuric acids were also obtained by the hydrolysis of O,N-disubstituted N-thiocyanohydroxylamines, it seemed certain that the first step in the latter hydrolysis must yield O,N-disubstituted hydroxylamine and hypothiocyanic acid. The production of hypothiocyanic acid indicates that the thiocyan group in O,N-disubstituted N-thiocyanohydroxylamine may be regarded as "positive," since it reacts in a manner similar to the "positive" halogen of the halogen amines[5]

$$R_2NCl + HOH \longrightarrow R_2NH + HOCl$$

On the other hand, alkaline hydrolysis of O,N-disubstituted N-thiocyanohydroxylamines gave products quite unlike those obtained in the alkaline hydrolysis of diethylthiocyanamine. Thus, the alkaline hydrolysis of the hydroxylamine derivatives proceeds according to the following reaction



$$RCH_2O\underset{\displaystyle R}{\underset{|}{N}}\text{—}SCN + KOH + H_2O \longrightarrow R\underset{\displaystyle O}{\underset{\|}{C}}\text{—}H + RNH_2 + K_2S_2O_3 + NH_3$$

while the alkaline hydrolysis of diethylthiocyanamine gave the following results[3]

$$(C_2H_5)_2N\text{—}SCN + KOH + H_2O \longrightarrow (C_2H_5)_2NH + KOCN + S$$

The presence of ammonia among the products of hydrolysis of hydroxylamine derivative may be explained by hydrolysis of potassium cyanate. The formation of potassium thiosulfate instead of sulfur may be explained since it has been shown by Lecher and co-workers that sulfur and potassium hydroxide react even in the cold to give thiosulfate and polysulfide. Taking into account these variations in the two reactions, it can be shown that the hydrolysis of O,N-disubstituted N-thiocyanohydroxylamines not only agrees with the theory of Lecher, Wittwer and Speer, but serves to support the mechanism of the hydrolysis advanced by them for thiocyanamine. They postulate, first, the formation of N,N-diethylthiohydroxylamine and then a chain splitting to give diethylamine and sulfur. If a similar reaction occurs in the case of O,N-disubstituted N-thiocyanohydroxylamine, the O,N-disubstituted thiohydroxylamine formed during the first step

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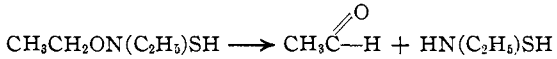
[4] Bjerrum and Kirschner, "Die Rhodanide des Goldes und das freie Rhodan," Kopenhagen, **1918**.

[5] Seliwanow, *Ber.*, **25**, 2621 (1892), Berg, *Ann. chim.*, [7] **3**, 341 (1894); W. A. Noyes, THIS JOURNAL, **23**, 460 (1901); Stieglitz, *ibid.*, **23**, 797 (1901); Jones, *ibid.*, **36**, 1268 (1914).

of the hydrolysis would certainly be unstable by virtue of the linking of the ethoxy group and the group SH to the same nitrogen atom. Since the ethoxy group is already in the state of oxidation comparable to an aldehyde,[6] it separates as aldehyde, leaving N-ethylthiohydroxylamine, and this, in turn, decomposes to give sulfur and ethylamine in accordance with the explanation of Lecher, Wittwer and Speer.

$$CH_3CH_2ON(C_2H_5)SCN + KOH \longrightarrow CH_3CH_2ON(C_2H_5)SH + KOCN$$



$$CH_3CH_2ON(C_2H_5)SH \longrightarrow CH_3\overset{\displaystyle O}{\overset{\Vert}{C}}—H + HN(C_2H_5)SH$$

$$\boxed{HN(C_2H_5)}\ S\ \boxed{H + HN(C_2H_5)}\ S\ \boxed{H + HN(C_2H_5)}\ S\ \boxed{H +} \cdots\cdots \longrightarrow H_2NC_2H_5 + S$$

In order to show that the formation of aldehyde could not be accounted for by the action of alkali upon the disubstituted hydroxylamine under the conditions of the experiment, sealed tubes containing the disubstituted hydroxylamine and 2% potassium hydroxide were heated at temperatures varying from 100 to 180° for periods of eight hours. In the case of O,N-diethylhydroxylamine no acetaldehyde or ethylamine could be detected below 150°. At 180° considerable quantities of acetaldehyde and ethylamine were formed. O,N-dibenzylhydroxylamine was not affected at 100°, but at 150° almost complete decomposition into benzaldehyde and benzylamine occurred.

Thiocyanamines

The only mention of the action of thiocyanogen upon primary amines,[7] other than the case of aniline already cited, was made by Söderbäck.[2] He stated that such reactions lead only to ill-defined products. In the present work, benzylamine and triphenylmethylamine were found to react with thiocyanogen to produce the corresponding thiocyanamine. The reaction proceeded as follows

$$2RNH_2 + (SCN)_2 \longrightarrow RNHSCN + RNH_3SCN$$

Pure triphenylmethylthiocyanamine was isolated by the action of triphenylmethylamine with thiocyanogen. Triphenylmethylthiocyanamine is a white, crystalline solid; m. p. 142°. It may be allowed to stand at room temperature for a week without serious decomposition. Benzylthiocyanamine, formed by the action of benzylamine with thiocyanogen, could not be isolated in the pure condition. It could neither be crystallized nor distilled. Analysis for nitrogen and sulfur gave values too low by 1–2% for benzylthiocyanamine, but its reactions with acids confirmed its structure.

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[6] Nef, *Ann.*, **280,** 328 (1894); Jones, THIS JOURNAL, **36,** 1285 (1914).

[7] Attention was directed to this type of reaction by what seemed to be a decomposition of O,N-dibenzyl-N-thiocyanohydroxylamine into benzaldehyde and benzylthiocyanamine. When O,N-dibenzyl-N-thiocyanohydroxylamine was first made considerable difficulty was experienced in crystallizing it. The oil possessed an odor not unlike that of benzaldehyde. Accordingly an attempt was made to prepare benzylthiocyanamine from benzylamine and thiocyanogen in order that the products of this suspected decomposition might be studied.

The reaction of thiocyanogen with primary amines to form thiocyanamines is of particular interest because it corresponds to the production of a monohalogen amine by the action of the halogen upon the amine in an inert solvent.

Action of Acids upon Thiocyanamines.—If the thiocyanamines are related to the monohalogen amines in this fashion, they should react with acids according to the following equation

$$\text{RNHSCN} + 2\text{HX} \longrightarrow \text{RNH}_3\text{X} + \text{XSCN}$$

The corresponding reaction of the monohalogen amines may be represented[8]

$$\text{RNHX} + 2\text{HX}' \longrightarrow \text{RNH}_3\text{X}' + \text{X—X}'$$

Thiocyanamines were found to undergo this reaction. When triphenylmethylthiocyanamine was dissolved in dry ether and treated with hydrochloric acid gas, triphenylmethylammonium chloride was precipitated. The ether filtrate, separated from the salt, was evaporated in a current of air and a heavy oil, which possessed a pungent odor, remained. This oil may be the monomolecular form of chlorothiocyanogen which Kaufmann[9] and Lecher[10] have been seeking, as it evaporated slowly and gave an intense red color when treated with a solution of ferric chloride.

Picric acid also reacts with triphenylmethylthiocyanamine to give triphenylmethylammonium picrate, but in this case the second product of the reaction is a yellow, amorphous substance which did not melt but gradually decomposed when heated.

Benzylthiocyanamine reacted similarly with hydrochloric and picric acids. The hydrochloride and the picrate were formed, respectively. In both these reactions the yellow, amorphous substance referred to above was obtained.

Rearrangement of Triphenylmethylthiocyanamine.—Further evidence that the thiocyanamines are related to the monohalogen amines may be had from the fact that triphenylmethylthiocyanamine undergoes the Stieglitz rearrangement.[11] Stieglitz and co-workers have succeeded in causing triphenylmethylbromo-amine, triphenylmethylhydroxylamine, triphenylmethylazide and *bis*-triphenylmethylhydrazine to rearrange; they obtained phenylimidobenzophenone from the rearrangement products. According to the theory advanced by Stieglitz, rearrangement in compounds of this type will be brought about by a reagent which removes a molecule of hydrobromic acid, water, nitrogen or ammonia, as the case may be, and gives rise to an intermediate, monovalent nitrogen compound. It is assumed that two electrons then shift from the methyl carbon atom

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[8] Berg, *Ann. chim.*, [7] **3**, 338 (1894); Vosburgh, THIS JOURNAL, **38**, 2086 (1916).

[9] Kaufmann and Liepe, *Ber.*, **57B**, 923 (1924); Kaufmann, *Ber.*, **60B**, 58 (1927).

[10] Lecher and Joseph, *Ber.*, **59B**, 2603 (1926).

[11] Stieglitz and Leech, THIS JOURNAL, **36**, 272 (1914); Vosburgh, *ibid.*, **38**, 2081 (1916); Senior, *ibid.*, **38**, 2718 (1916); Stieglitz and Senior, *ibid.*, **38**, 2727 (1916); Stieglitz and Brown, *ibid.*, **44**, 1270 (1922); Stieglitz, *ibid.*, **44**, 1293 (1922).

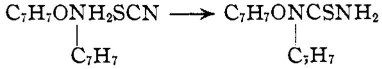
of the triphenylmethyl radical to the nitrogen atom, followed by a migration of a phenyl group from the carbon atom to the nitrogen atom; the final product of the rearrangement is phenylimidobenzophenone. This reaction may be represented in the case of triphenylmethylthiocyanamine as follows

$$(C_6H_5)_3CNHSCN \xrightarrow{-HSCN} (C_6H_5)_3C-N \longrightarrow (C_6H_5)_2C{=}N(C_6H_5)$$

Triphenylmethylthiocyanamine was found to undergo this rearrangement when it was mixed with calcium oxide and heated at a temperature between 440 and 450° for a very short time. The phenylimidobenzophenone produced by this rearrangement was identified by the products of its acid hydrolysis, namely, aniline and benzophenone.

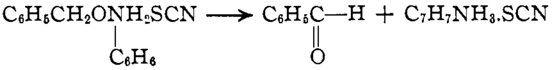
Attempts to use other reagents to produce this rearrangement did not succeed. Soda lime converted triphenylmethylthiocyanamine almost quantitatively into triphenylmethylamine. Mercuric oxide, lead oxide and sodium methylate were also tried.

Formation of Ureas from Substituted Ammonium Thiocyanates.—The O,N-dibenzylhydroxylammonium thiocyanate formed in the preparation of O,N-dibenzyl-N-thiocyanohydroxylamine was found to undergo two interesting transformations. When this salt was suspended in water and the water removed by evaporation, the usual transformaton occurred and α,α'-benzylbenzyloxythiourea was the product.



$$C_7H_7O\underset{\substack{|\\ C_7H_7}}{N}H_2SCN \longrightarrow C_7H_7O\underset{\substack{|\\ C_7H_7}}{N}CSNH_2$$

This compound was found to be the same as that prepared by evaporation of a suspension of O,N-dibenzylhydroxylamine hydrochloride and potassium thiocyanate; but when O,N-dibenzylhydroxylammonium thiocyanate was heated for fifteen minutes at 150° previous to its treatment with water, no α,α'-benzylbenzyloxythiourea could be obtained; the products isolated were benzylthiourea and benzaldehyde. The following reaction represents these changes



$$C_6H_5CH_2O\underset{\substack{|\\ C_6H_6}}{N}H_2SCN \longrightarrow C_6H_5\underset{\substack{\|\\ O}}{C}-H + C_7H_7NH_3.SCN$$

$$C_7H_7NH_3SCN \longrightarrow C_7H_7NHCSNH_2$$

Efforts to convert triphenylmethylammonium thiocyanate into the corresponding thiourea by this method failed. Heat brought about decomposition and evaporation with water caused hydrolysis of the salt. Triphenylmethylcarbinol was isolated from the products of hydrolysis.

Experimental Part

O,N-Diethyl-N-thiocyanohydroxylamine, $(C_2H_5O)(C_2H_5)NSCN$

Preparation of O,N-Diethyl-N-thiocyanohydroxylamine.—A suspension of 11.3 g. of lead thiocyanate in 50 cc. of absolute ether was treated with 4.8 g. of bromine. The mixture was shaken until the color of bromine disappeared and then filtered into an ice-cooled ether (50 cc.) solution of 9.2 g. of O,N-diethylhydroxylamine, prepared by the method of Hecker[12] as modified by Major and Fleck.[13] Reaction took place at once and 4.0 g. of O,N-diethylhydroxylammonium thiocyanate separated as an oil. The ether was removed rapidly by means of diminished pressure. During this operation the temperature of the flask was not allowed to rise above 0 °. The oil which remained distilled at 45–46 ° under 2 mm. A liquid air trap interposed between the receiver and the oil pump greatly facilitated the maintenance of this pressure; yield, 40%.

Anal. Subs., 0.0988: $BaSO_4$, 0.1559. Subs., 0.0536: N_2, 9.0 cc. (20 °, 759.6 mm.). Calcd. for $C_5H_{10}ON_2S$: S, 21.92; N, 19.15. Found: S, 21.87; N, 19.5.

Acid Hydrolysis of O,N-Diethyl-N-thiocyanohydroxylamine.—One g. of O,N-diethyl-N-thiocyanohydroxylamine was added to 100 cc. of ice-cooled 2% hydrochloric acid and the mixture kept in the ice box until the oil dissolved. The solution was then distilled and hydrocyanic acid and thiocyanic acid were found in the distillate. A test for sulfate was obtained from the residue of the distillation. The remainder of this residue was made alkaline and distilled. The distillate was extracted with benzene and treated with phenylisocyanate. The crystals which separated melted at 63 °. When mixed with α-phenyl β,β'-ethylethoxyurea, $(C_2H_5O)(C_2H_5)N{\cdot}CONH(C_6H_5)$, prepared by the method of Jones and Major,[14] the melting point was unchanged.

Alkaline Hydrolysis of O,N-Diethyl-N-thiocyanohydroxylamine.—One g. of O,N-diethyl-N-thiocyanohydroxylamine was added to 100 cc. of an ice-cooled 2% solution of potassium hydroxide and the mixture allowed to stand in an ice box for two days. The solution was then distilled. The distillate contained acetaldehyde and ethylamine.

The residual liquid of this distillation contained no free sulfur but gave the ordinary tests for thiosulfate. To precipitate lead thiosulfate, calcium nitrate was added to the remainder of the residue, the solution filtered, the color of phenolphthalein in the filtrate discharged by acetic acid and the salt obtained by the addition of lead nitrate.

Anal. Subs., 0.1272: $PbSO_4$, 0.1220. Subs., 0.0606: 19.0 cc. of 0.01 N I_2 solution. Calcd. for PbS_2O_3: Pb, 64.99; S, 20.06. Found: Pb, 65.5; S, 20.0.

The distillate, which contained acetaldehyde and ethylamine, was acidified with hydrochloric acid and the acetaldehyde removed by distillation. This distillate was treated with an acetic acid solution of *p*-nitrophenylhydrazine. The yellow plates which separated melted at 127.5 °. Mixing with acetaldehyde-*p*-nitrophenylhydrazone[15] did not alter this melting point. This established the formation of acetaldehyde.

The residual liquid, which contained the hydrochloride of ethylamine, was made alkaline and distilled. Addition of ethyl oxalate to a portion of the distillate yielded colorless needles which melted at 178 °. The melting point was not changed when mixed with diethyloxamide.[16] This established the presence of ethylamine. The remainder of this distillate was acidified with hydrochloric acid and evaporated to dryness. Ammonium chloride was found to be present.[17]

O,N-Dibenzyl-N-thiocyanohydroxylamine, $(C_7H_7O)(C_7H_7)NSCN$

Preparation of O,N-Dibenzylcarbethoxyhydroxamic Ester.—To 59 g. of carbethoxy-

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[12] Hecker, *Am. Chem. J.*, **50**, 451 (1913).

[13] Major and Fleck, THIS JOURNAL, **50**, 1479 (1928).

[14] Jones and Major, *ibid.*, **49**, 1538 (1927).

[15] Hyde, *Ber.*, **32**, 1813 (1899).

[16] Schiff, *Ber.*, **17**, 1034 (1884).

[17] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, Vol. II, p. 39.

hydroxamic acid, prepared by the method of Jones,[18] 151 g. of benzyl chloride and 66 g. of potassium hydroxide, dissolved in alcohol, were added. The solution grew warm at once and potassium chloride separated. After twenty-four hours, the mixture was refluxed for one hour, then cooled and filtered. The alcohol was distilled and the residue diluted with water and extracted with ether. The ether solution was washed with dilute sodium hydroxide to remove any O-benzylcarbethoxyhydroxamic ester. Five g. of this substance, b. p. 171–172° under 7 mm., was recovered. The neutral portion remaining with the ether was dried with sodium sulfate. Distillation of the ether left a colorless oil which was fractionated. The fraction boiling between 200 and 203° under 7 mm. was collected; yield, 90 g.

Anal. Subs., 0.2652: N_2, 11.3 cc. (21°, 761.2 mm.). Calcd. for $C_{17}H_{19}O_3N$: N, 4.91. Found: 4.95.

Preparation of O,N-Dibenzylhydroxylamine.—A solution of 63 g. of O,N-dibenzylcarbethoxyhydroxamic ester was added to 25 g. of sodium hydroxide dissolved in 200 cc. of 50% alcohol and the mixture refluxed for one hour. After distillation of the alcohol, the O,N-dibenzylhydroxylamine was extracted with ether and the extract dried with sodium sulfate. The colorless oil which remained after removal of the ether distilled at 145–146° under 3 mm.; yield, 41 g.

Preparation of O,N-Dibenzyl-N-thiocyanohydroxylamine.—A suspension of 8.0 g. of lead thiocyanate in 50 cc. of absolute ether was treated with 3.8 g. of bromine. The mixture was shaken until the color of bromine disappeared and then filtered into an ice-cooled solution of 10 g. of O,N-dibenzylhydroxylamine in ether. Reaction took place at once and 5.9 g. of O,N-dibenzylhydroxylammonium thiocyanate crystallized. This salt was collected on a filter and recrystallized by dissolving it in a large amount of absolute ether and evaporating the ether under diminished pressure; m. p. 91°.

Anal. Subs., 0.1190: $BaSO_4$, 0.0988. Subs., 0.1450: N_2, 13.4 cc. (25°, 753.0). Calcd. for $C_{15}H_{16}ON_2S$: S, 11.75; N, 10.33. Found: S, 11.43; N, 10.48.

The ether filtrate, separated from the salt, was evaporated under diminished pressure to 10 cc. The second crop of O,N-dibenzylhydroxylammonium thiocyanate which separated during this process was removed by filtration and the filtrate was kept under a high vacuum at room temperature for three hours. The product remained as an oil but it finally crystallized when cooled in ice. Scratching the side of the containing vessel greatly facilitated this crystallization. The crystals were triturated with 5 cc. of absolute alcohol, filtered and washed with a small amount of cold dry ether; m. p. 50–52°; yield, 47%.

Anal. Subs., 0.2098: $BaSO_4$, 0.1746. Subs., 0.1422: N_2, 12.6 cc. (18°, 752.7). Calcd. for $C_{15}H_{14}ON_2S$: S, 11.85; N, 10.37. Found: S, 11.4; N, 10.3.

Acid Hydrolysis of O,N-Dibenzyl-N-thiocyanohydroxylamine.—One g. of O,N-dibenzyl-N-thiocyanohydroxylamine was dissolved in 100 cc. of a solution of 2% hydrochloric acid in 75% alcohol. The mixture grew warm and was distilled at once. Hydrocyanic and thiocyanic acids were found in the distillate. When the residue from this distillation was cooled, O,N-dibenzylhydroxylamine hydrochloride precipitated. Evaporation of the filtrate, separated from the salt, yielded more of this salt. A total of 0.95 g. of O,N-dibenzylhydroxylamine hydrochloride was obtained from this hydrolysis. The base was freed with sodium hydroxide, extracted with benzene and treated with phenylisocyanate. The benzene was removed by a current of air and the product purified by dissolving in alcohol and precipitating with water; m. p. 107°. The melting point remained unaltered when mixed with α-phenyl-β,β'-benzylbenzyloxyurea.[19]

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[18] Jones, *Am. Chem. J.*, **20**, 39 (1898).

[19] Beckmann, *J. prakt. Chem.*, [2] **56**, 77 (1897).

Sulfate was found in the filtrate from which O,N-dibenzylhydroxylamine hydrochloride had been removed.

Alkaline Hydrolysis of O,N-Dibenzyl-N-thiocyanohydroxylamine.—One g. of O,N-dibenzyl-N-thiocyanhydroxylamine was refluxed with 100 cc. of a 2% solution of potassium hydroxide for half an hour. A reddish solid formed. The products of hydrolysis were separated by the method used in the case of the corresponding ethyl compound. Benzaldehyde was identified by conversion into benzalphenylhydrazone and determination of the melting point when mixed with benzalphenylhydrazone prepared by the method of Behrend and Leuchs.[20]

Benzylamine was identified by extraction of the free base with benzene and conversion into α,β-phenylbenzylurea; m. p. 165°. When mixed with α,β-phenylbenzylurea prepared by the method of Ley and Kraft,[21] the melting point was not lowered. Thiosulfate was shown to be present by the usual qualitative tests.

Alkaline Decomposition of O,N-Disubstituted Hydroxylamines

Decomposition of O,N-diethylhydroxylamine.—One g. of O,N-diethylhydroxylamine was heated in a sealed tube with 100 cc. of a 2% solution of potassium hydroxide for eight hours. The contents of the tube were then distilled and the distillate was tested for aldehyde with Schiff's reagent. A negative test was obtained from a tube heated at 100°. At 150° only a slight amount of aldehyde was found, while at 180° almost complete decomposition took place. The contents of the tube heated at 180° was acidified with hydrochloric acid and the acetaldehyde removed by distillation. Yellow plates m. p. 127.5°, separated when the distillate was treated with *p*-nitrophenylhydrazine. When mixed with acetaldehyde-*p*-nitrophenylhydrazone it melted at 127.5°.

The residual liquid from this distillation was made alkaline and the ethylamine removed by distillation. Treatment of this distillate with ethyl oxalate gave white needles; m. p. 178°. Mixing with diethyloxamide produced no change in the melting point.

Decomposition of O,N-Dibenzylhydroxylamine.—One g. of O,N-dibenzylhydroxylamine was sealed in a tube with 100 cc. of a 2% solution of potassium hydroxide. This solution heated for eight hours at 100° showed no change. When it was heated at 150° for a similar time, almost complete decomposition ensued. The products of this decomposition were separated as in the case of the diethyl compound. Benzaldehyde was identified by conversion into benzalphenylhydrazone; m. p. 155°. When mixed with benzalphenylhydrazone[20] it melted at 155–156°.

The residual liquid, which contained benzylamine hydrochloride, was made alkaline, extracted with benzene and the benzene solution treated with phenylisocyanate. The white crystals which separated melted at 169°. A mixture with α,β-phenylbenzylurea[21] showed no lowering of melting point.

Triphenylmethylthiocyanamine, $(C_6H_5)_3CNHSCN$

Preparation of Triphenylmethylthiocyanamine.—A suspension of 6.6 g. of lead thiocyanate in 50 cc. of absolute ether was treated with 3.2 g. of bromine. The mixture was shaken until the color of bromine disappeared and then filtered into a solution of 10.4 g. of triphenylmethylamine in 150 cc. of dry ether. The amine was prepared by the method of Elbs,[22] as modified by Vosburgh.[23] Immediate reaction, accompanied by the separation of 5.6 g. of triphenylmethylammonium thiocyanate, took place. This salt was collected on a filter and recrystallized from benzene by addition of ligroin; m. p. 173°.

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[20] Behrend and Leuchs, *Ann.*, **257**, 227 (1890).

[21] Ley and Kraft, *Ber.*, **40**, 703 (1907).

[22] Elbs, *Ber.*, **17**, 702 (1884).

[23] Vosburgh, THIS JOURNAL, **38**, 2085 (1916).

Anal. Subs., 0.1630: $BaSO_4$, 0.1174. Subs., 0.1596: N_2, 12.2 cc. (23°, 750.5). Calcd. for $C_{20}H_{18}N_2S$: S, 10.06; N, 8.80. Found: S, 9.89; N, 8.76.

The ether filtrate, separated from the salt, was evaporated to dryness. The sticky solid which resulted was triturated with 10 cc. of carbon tetrachloride and the solution filtered. Triphenylmethylthiocyanamine was recrystallized from absolute ether by addition of ligroin (b. p. 30–60°); m. p. 142°; yield, 55%.

Anal. Subs., 0.1378: $BaSO_4$, 0.1038. Subs., 0.1446: N_2, 11.7 cc. (26°, 743.9). Calcd. for $C_{20}H_{16}N_2S$: S, 10.13; N, 8.86. Found: S, 10.36; N, 9.05.

Rearrangement of Triphenylmethylthiocyanamine.—A mixture of 0.5 g. of triphenylmethylthiocyanamine and 1.0 g. of freshly ignited calcium oxide was heated in a dry 60cc. Pyrex Erlenmeyer flask immersed in a metal-bath at 440–450° for one minute. Considerable decomposition occurred at this temperature and the odor of ammonia was apparent. The product was dissolved in ether, the solution filtered from the lime and the ether filtrate refluxed with an excess of dilute hydrochloric acid for half an hour. The two layers were separated, the water solution was extracted three times with ether and each ether extract washed with dilute hydrochloric acid. The original ether solution was washed twice with dilute hydrochloric acid. The acid portions were united (A) as were also the ether portions (B).

The acid solution (A) was made strongly alkaline and distilled with steam into dilute hydrochloric acid. This solution was evaporated to dryness on a water-bath. The resulting solid, 0.042 g., was treated with a few drops of a strong solution of sodium hydroxide and the aniline extracted with benzene. Addition of α-naphthylisocyanate caused *sym.*-α-naphthylphenylurea to separate m. p. 221–223°. No lowering in melting point was observed when this product was mixed with *sym.*-α-naphthylphenylurea prepared by the method of Dixon.[24]

Most of the ether was distilled from the ether solution (B) and the remainder was distilled with steam. The distillate was extracted with ether and the ether removed *in vacuo.* By this method 0.082 g. of benzophenone, m. p. 25–30°, was obtained. This benzophenone was converted into the corresponding oxime by the method given in Mulliken;[25] m. p. 141–142°. The melting point was not changed when mixed with benzophenone-oxime prepared from pure benzophenone.

Benzylthiocyanamine, $C_6H_5CH_2NHSCN$

Preparation of Benzylthiocyanamine.—A suspension of 6.6 g. of lead thiocyanate in 25 cc. of absolute ether was treated with 3.2 g. of bromine. The mixture was shaken until the color of bromine disappeared and then filtered into a solution of 4.3 g. of benzylamine dissolved in 25 cc. of dry ether. Reaction took place at once and 3.5 g. of benzylammonium thiocyanate separated. This salt was recrystallized from ethyl acetate by addition of ligroin; m. p. 100–101°. No lowering of the melting point of this salt could be detected when it was mixed with benzylammonium thiocyanate prepared by the method of Dixon.[26]

The filtrate, separated from the salt, was evaporated under diminished pressure. When practically all of the ether was removed, the heavy oil was subjected to a high vacuum for five hours. Crystallization could not be brought about and complete decomposition accompanied any attempt to distil this oil. Analysis for nitrogen and sulfur gave results too low by 1–2% for the calculated values. Change of reaction

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[24] Dixon, *Proc. Chem. Soc.*, **16**, 208 (1900).

[25] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, Vol. I, p. 150.

[26] Dixon, *J. Chem. Soc.*, **59**, 553 (1891).

solvent, washing the reaction products with ice water, etc., did not improve the purity of the benzylthiocyanamine materially.

Action of Acids upon Benzylthiocyanamine.—One g. of benzylthiocyanamine was dissolved in absolute ether and dry hydrochloric acid gas passed into the solution. Benzylammonium chloride separated at once along with a yellow, amorphous substance. The benzylammonium chloride was converted into α,β-phenylbenzylurea and identified by mixed melting point determinations.

One g. of benzylthiocyanamine was dissolved in absolute ether and an absolute ether solution of picric acid added. The reaction proceeded slowly but was complete within one hour. A yellow, amorphous substance also separated from the solution. The benzylammonium picrate was freed from this substance by recrystallization from ethyl acetate by addition of ligroin; m. p. 200–201°. Mixed melting points proved this compound to be identical with benzylamine picrate prepared by addition of an absolute ether solution of picric acid to an absolute ether solution of benzylamine.

α,α′-Benzylbenzyloxyureas, $(C_7H_7O)(C_7H_7)N{\cdot}CONH_2$

Preparation of α,α′-benzylbenzyloxyurea.—A solution containing 2 g. of O,N-dibenzylhydroxylamine hydrochloride and 0.7 g. of potassium cyanate in 50 cc. of water was evaporated to dryness. The heavy oil which resulted was dissolved in alcohol and precipitated with water. The urea formed as an oil which solidified in long needles after several days. It was recrystallized from ligroin; m. p. 98–99°; yield, 30%.

Anal. Subs., 0.1134: N_2, 10.6 cc. (21°, 741.8). Calcd. for $C_{15}H_{16}O_2N_2$: N, 10.93. Found: 10.6.

Preparation of α,α′-benzylbenzyloxythiourea, $(C_7H_7O)(C_7H_7)N{\cdot}CS{\cdot}NH_2$.—To prepare this thiourea, the calculated amount of O,N-dibenzylhydroxylamine hydrochloride and potassium thiocyanate, dissolved in water, was treated as outlined in the previous experiment. The thiourea crystallized in plates; m. p. 94–95°; yield, 24%.

Anal. Subs., 0.1132: N_2, 10.8 cc. (24°, 753.3). Calcd. for $C_{15}H_{16}ON_2S$: N, 10.63. Found: 10.88.

Formation of Ureas from Substituted Ammonium Thiocyanates.—Two g. of O,N-dibenzylhydroxylammonium thiocyanate was suspended in 50 cc. water and the suspension evaporated to dryness. The oil which remained was dissolved in alcohol and precipitated by water. The α,α′-benzylbenzyloxythiourea was recrystallized from ligroin; m. p. 94–95°; yield, 31%. The melting point was not changed when this substance was mixed with α,α′-benzylbenzyloxythiourea prepared from O,N-dibenzylhydroxylamine hydrochloride.

One-half g. of O,N-dibenzylhydroxylammonium thiocyanate was subjected to dry distillation. The pressure was maintained at 20 mm. and the temperature of the metal-bath surrounding the distilling flask was kept between 150 and 160°. The distillate contained benzaldehyde which was identified by conversion into benzalphenylhydrazone and determination of the melting point when mixed with synthetic benzalphenylhydrazone.

The residue from the above distillation was dissolved in alcohol and precipitated carefully with water. The resulting solid was recrystallized from a large amount of boiling water. The benzylthiourea prepared in this manner melted at 147–148°. When mixed with benzylthiourea, prepared by the method of Dixon,[26] no lowering of melting point could be detected.

Summary

1. O,N-diethyl-N-thiocyanohydroxylamine and O,N-dibenzyl-N-thiocyanohydroxylamine have been prepared by the action of thiocyanogen on

the corresponding O,N-disubstituted hydroxylamines. The structure of these compounds has been proven by hydrolysis.

2. O,N-dibenzylhydroxylammonium thiocyanate was found to transform into α,α'-benzylbenzyloxythiourea when a solution of it in water was evaporated. When O,N-dibenzylhydroxylammonium thiocyanate was heated in the absence of water, benzylthiourea and benzaldehyde were the products.

3. Triphenylmethylthiocyanamine and benzylthiocyanamine have been prepared by the action of thiocyanogen on triphenylmethylamine and benzylamine, respectively. These compounds have been shown to resemble monohalogen amines in their chemical behavior.

4. Triphenylmethylthiocyanamine was found to undergo the Stieglitz rearrangement when heated with calcium oxide. Phenylimidobenzophenone was shown to be a product of rearrangement.

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[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE ACIDS OF MAPLE SUGAR "SAND"

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Maple sugar "sand" is the deposit of the calcium salts of organic acids, chiefly calcium malate, which forms in the evaporating kettle during the concentration of maple sap. The acids of maple sugar "sand" have been investigated by v. Lippmann,[1] who found, in addition to *l*-malic acid, considerable *d*-tartaric acid and a small quantity of tricarballylic acid. V. Lippmann gives very little information regarding his method of procedure in separating these acids except that tricarballylic acid was extracted from the acid mixture by means of ether.

Van Zoeren,[2] attempting to confirm v. Lippmann's results, obtained sufficient tartaric acid to identify microscopically as acid potassium salt but was unable to isolate tricarballylic acid.

An investigation of a sample of maple "sand" was made in the Food Research Division. The volatile acids were identified as a mixture of formic and acetic acids. In addition to *l*-malic acid, fumaric, succinic and citric acids were separated in small quantities. Traces of *d*-tartaric acid and tricarballylic acid were identified by crystallographic[3] examination of the proper fractions, though it was impossible to separate these acids in a state of purity sufficient for the determination of melting points.

[1] E. O. v. Lippmann, *Ber.*, **47**, 3094 (1914).

[2] Van Zoeren, *Trans. Roy. Soc. Canada* (3) **13**, 222 (1919).

[3] Crystallographic examinations were made by G. L. Keenan of the Food, Drug and Insecticide Administration.